



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of  
Kouji KUBOTA et al.

Docket No: Q79788

Appln. No.: 10/772,427

Group Art Unit: 1762

Confirmation No.: 2054

Examiner: Ermac Cameron

Filed: February 6, 2004

For: TREATMENT COMPRISING WATER- AND OIL-REPELLENT AGENT

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Kouji KUBOTA, hereby declare and state:

THAT I am a citizen of Japan;

THAT I have received the degree of master of chemical engineering in March 1993 from Yamaguchi University;

THAT I have been employed by DAIKIN INDUSTRIES LTD. since April 1, 1993, where I hold a position as researcher, with responsibility for research works on the development of the synthesis of fluorine-containing compound and the development of water and oil-repellent; and

THAT I am familiar with the Office Action dated August 12, 2005.

I report below on certain experimentation that was conduct by me or under my direct supervision.

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**U.S. Application No.: 10/772,427**

**EXPERIMENTATION**

Test procedures of the fluorine adhesion rate, the water-repellency and the oil-repellency are as follows.

**Fluorine adhesion rate**

A combustion flask is sufficiently washed with pure water. Then, 15 mL of pure water is charged into the combustion flask, and the weight of the flask containing water is measured. The weight of pure water is determined by deducting a previously measured weight of the combustion flask from the weight of flask containing water. A platinum basket is heated twice or thrice to fully evaporate water. 75 mg of a carpet pile is weighed on a KIMWIPE, which is folded with enclosing a combustion aid (30 mg) and is positioned in a platinum basket. Oxygen is blown into the combustion flask, and the piles are burned and decomposed, and absorbed into pure water contained in the flask. After the absorption for 30 minutes, 10 mL of an absorption liquid and 10 mL of a buffer liquid (50 mL of acetic acid, 50 g of sodium chloride, 0.5 g of trisodium citrate dihydrate, and 32 g of sodium hydroxide are added to water to give a total amount of 1L) are charged into a plastic cup and an F ion is measured by an F ion meter with sufficiently stirring. A fluorine adhesion amount and a fluorine adhesion rate are calculated according to the following equations.

Fluorine adhesion amount [ppm] =

(Measurement value [ppm] - Blank measurement value [ppm]) x (Pure water weight [g]/Pile weight [mg]) x 1000

Fluorine adhesion rate (%) = (Fluorine adhesion amount after steam treatment, water wash, centrifugal dehydration and thermal curing treatment [ppm])/(Fluorine adhesion amount immediately after squeezed so that WPU (wet pick up) is 400% or 300% [ppm])

The fluorine adhesion rate is shown as "Exhaustability" in the following Tables.

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**Water-repellency**

A carpet treated with a water- and oil-repellent agent is stored in a thermo-hygrostat having a temperature of 21°C and a humidity of 65% for at least 4 hours. A test liquid (isopropyl alcohol (IPA), water, and a mixture thereof, as shown in Table I) which has been also stored at 21°C is used. The test is conducted in an air-conditioned room having a temperature of 21°C and a humidity of 65%. Droplets of the test liquid in an amount of 50 µL (5 droplets) are softly dropped by a micropipette on the carpet. If 4 or 5 droplets remain on the carpet after standing for 10 seconds, the test liquid passes the test. The water-repellency is expressed by a point corresponding to a maximum content of isopropyl alcohol (% by volume) in the test liquid which passes the test. The water-repellency is evaluated as sixteen levels which are Fail, 0, 0.2, 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, 9 and 10 in order of a bad level to an excellent level.

**Table I Water-repellency test liquid**

Point	(% by volume)	
	Isopropyl alcohol	Water
10	100	0
9	90	10
8	80	20
7	70	30
6	60	40
5	50	50
4	40	60
3	30	70
2.5	25	75
2	20	80
1.5	15	85
1	10	90
0.5	5	95
0.2	2	98
0	0	100
Fail	Inferior to isopropyl alcohol 0/water 100	

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**Oil-repellency**

A carpet treated with a water- and oil-repellent agent is stored in a thermo-hygrostat having a temperature of 21°C and a humidity of 65% for at least 4 hours. A test liquid (shown in Table II) which has been also stored at 21°C is used. The test is conducted in an air-conditioned room having a temperature of 21°C and a humidity of 65%. Droplets of the test liquid in an amount of 50 µL (5 droplets) are softly dropped by a micropipette on the carpet. If 4 or 5 droplets remain on the carpet after standing for 30 seconds, the test liquid passes the test. The oil-repellency is expressed by a point corresponding to a maximum content of isopropyl alcohol (% by volume) in the test liquid which passes the test. The oil-repellency is evaluated as nine levels which are Fail, 1, 2, 3, 4, 5, 6, 7 and 8 in order of a bad level to an excellent level.

**Table II Oil-repellency test**

Point	Test liquid	Surface tension (dyne/cm, 25°C)
8	n-Heptane	20.0
7	n-Octane	21.8
6	n-Decane	23.5
5	n-Dodecane	25.0
4	n-Tetradecane	26.7
3	n-Hexadecane	27.3
2	Mixture liquid of n-Hexadecane 35/nujol 65	29.6
1	Nujol	31.2
Fail	Inferior to 1	-

The water- and oil-repellent compositions were prepared as follows:

**Preparative Experiment 1**

$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{COOCH}=\text{CH}_2$  (a mixture of compounds wherein n is 3, 4 and 5, the average of n is 3.1) (150 g), 2-ethylhexyl acrylate (40 g), 3-chloro-2-hydroxypropyl methacrylate (2 g), n-lauryl mercaptan (1 g), polyoxyethylene(21)laurylether (20 g), dialkyldimethyl ammonium chloride (10 g), tripropylene glycol (75 g) and ion exchanged water (480 g) were mixed to prepare a

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mixture liquid. This mixture liquid was heated to 60°C and then homogenized by a high pressure homogenizer. The resultant emulsified liquid was charged into 1 L autoclave, the atmosphere of the autoclave was replaced with nitrogen to remove the dissolved oxygen. A vinyl chloride monomer (70 g) having the purity of 99% was charged and then 2,2'-azobis(2-amidinopropane) dihydrochloride (2 g) was charged. The copolymerization was performed at 60°C for 8 hours with stirring to give a fluorine-containing copolymer emulsion. The copolymer emulsion was diluted with ion exchanged water to prepare a fluorine-containing acrylate-based water- and oil-repellent aqueous composition having a solid content of 30% by weight. The composition of the resultant polymer was almost the same as the composition of the charged monomers. The composition of the copolymer emulsion is shown in Table I.

**Preparative Experiments 2 and 3**

The ingredients shown in Table I were used to prepare a fluorine-containing acrylate-based water- and oil-repellent aqueous composition having a solid content of 30% by weight.

Table I

	Preparative Experiment 1		Preparative Experiment 2		Preparative Experiment 3	
	Composition 1		Composition 2		Composition 3	
	Mole %	Mass (g)	Mole %	Mass (g)	Mole %	Mass (g)
CF <sub>3</sub> CF <sub>2</sub> (CF <sub>2</sub> CF <sub>2</sub> ) <sub>n</sub> (CH <sub>2</sub> ) <sub>2</sub> COOCH=CH <sub>2</sub> n=3,4,5	17%	150	17%	149	17%	149
Methacrylic acid			10%	14	15%	21
Vinyl chloride monomer	69%	70	60%	61	56%	57
2-Ethylhexylacrylate	13%	40	12%	35	11%	33
3-Chloro-2-hydroxypropyl methacrylate	1%	2	1%	2	1%	2
n-Lauryl mercaptan		1		1		1
Polyoxyethylene(21)lauryl ether		20		20		20
Dialkyldimethyl ammonium chloride		10		10		10
2,2'-Azobis(2-amidinopropane) dihydrochloride		2		2		2
Tripropylene glycol		75		75		75
Ion exchanged water		480		480		480

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The properties of the fluorine-containing acrylate-based water- and oil-repellent aqueous compositions were determined as follows:

**Experiments 1 to 3**

The fluorine-containing acrylate-based water- and oil-repellent aqueous composition (Composition 1, 2 or 3) (0.96 g) prepared in each of Preparative Experiments 1 to 3, a 30 % aqueous solution (0.04 g) of polyallylamine hydrochloride having a molecular weight of 15,000, water (993.0 g), and a stain blocking agent (a mixture of phenol/formaldehyde condensate and polymethacrylic acid in a weight ratio of 50:50) (hereinafter referred to as "SB agent") (6.0 g) were mixed to prepare a mixture liquid and a 10 % aqueous solution of sulfamic acid was added so that the mixture had pH of at most 2 to give a treatment liquid.

A carpet (15 cm x 5 cm, nylon-6, cut pile, density of 32oz/yd<sup>2</sup>) which was washed with water and dehydrated to WPU of 25% (WPU: wet pick up; when 100 g of the carpet absorbs 25 g of a liquid, WPU is 25%) was immersed in the above-mentioned treatment liquid for 30 seconds so that WPU was 250%. Then, a normal-pressure steamer treatment (temperature: 100°C to 107°C) was conducted for 60 seconds under the state that a pile surface was upward. The carpet was lightly rinsed with 2 L of water and then centrifugal dehydration was conducted to give a WPU amount of 25%. Finally, the carpet was thermally treated at 110°C for 10 minutes.

The resultant carpet was subjected to a fluorine adhesion rate measurement, a water-repellency test and an oil-repellency test. The results are shown in Table II.

**Table II**

	Experiment 1	Experiment 2	Experiment 3
Composition 1	0.96 g	-	-
Composition 2	-	0.96 g	-
Composition 3	-	-	0.96 g
Polyallylamine hydrochloride	0.04 g	0.04 g	0.04 g
SB agent	6.00 g	6.00 g	6.00 g
Exhaustability (Fluorine adhesion rate) (%)	81	83	84
Water repellency	8	5	4
Oil repellency	5	3	3

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The addition of the polyallylamine hydrochloride gives a high fluorine adhesion rate as shown in Experiments 1, 2 and 3, but the introduction of carboxyl group (that is, methacrylic acid) into a polymer constituting the water- and oil-repellent agent deteriorates water repellency and oil repellency.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 1 - Dec. - 2005

  
Kouji Kubota  
Kouji KUBOTA